

## MILITARY WATER PURIFICATION MEMBRANE TECHNOLOGY DEVELOPMENT

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Potable water is one of the Army and Marine Corp's most basic logistics requirements, particularly in arid environments. The core technology in the Army and Marine Corp fielded tactical water purification units is reverse osmosis. New integrated membranes systems are under development combining membrane pretreatment with reverse osmosis. While the current systems have provided the Army with the capability to purify any source water with sufficient quality and quantities to support deployed troops, improvements are needed in membrane technology and systems to reduce the size and weight of the systems, reduce power, improve resistance to fouling, and improve rejection of potential chemical threat agents. The U.S. Army, Office of Naval Research, and Defense Research Project Agency are conducting collaborative research efforts to develop new membranes, new pretreatment technology, and new membrane system concepts to address the limitations of current technology for military water purification applications.

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## BACKGROUND

Potable water is one of the Army's most basic logistics requirements, particularly in arid environments. It directly affects the health and welfare of the individual soldier as well as the combat readiness of committed forces. During World War I, health problems associated with poor drinking water quality prompted the U.S. Army to address the issue of providing potable drinking water to the field. The principal piece of equipment developed was the "Mobile Water Purification Unit" featuring sand filtration and chlorination. During World War II, it became increasingly apparent that this technology was only partially effective in providing potable and uncontaminated water for drinking, washing, culinary, bathing and laundering purposes. Subsequent to World War II, a complete line of water purification equipment, each designed for use on a different type of source water was developed and fielded. During the 1960's, the Army realized that although these units provided potable water, there was, from a logistical and training standpoint, a distinct need for a single water purification unit capable of purifying raw fresh water, seawater and brackish water. In addition, there was now a need to purify water contaminated with nuclear, biological and chemical (NBC) warfare agents. Consequently, the Army funded research in reverse osmosis technology which resulted in the development and procurement of two systems, the 600 and 3,000 gallon per hour (GPH) reverse osmosis water purification units (ROWPUs). They were fielded in 1981 and 1989 respectively, and are still used today by the Army, Marine Corps, and Air Force.

The use of reverse osmosis as the military's core technology has recently been reinforced because of its ability to desalinate and since it is effective against a wide array of potential contaminants. Increased terrorist activity in the United States and the deployment of the military throughout the world has heightened the concern within the military for better protection of potable water sources, purification systems, and distribution systems from contamination. There is the potential that water sources may be contaminated with disease causing organisms, a rapidly expanding list of toxic industrial chemicals, pesticides and herbicides from agricultural activities, chemical warfare agents, or agents of opportunity introduced by terrorist activities. The ability of the military to monitor these contaminants in both the source and finished drinking water is extremely limited. Monitoring chemical contaminants down to the drinking water limits is time consuming and requires laboratories with sophisticated equipment. It is not currently feasible to do these types of analysis in military field environments. Since the military cannot adequately monitor all the potential contaminants in potential water sources it must rely on purification technology to ensure the safety of the soldier's drinking water. RO is considered a best available treatment technique by the military and Environmental Protection Agency for most classes of chemicals and the primary reason it is not recommended for many water treatment applications is the high capital and operating costs and high operator skill required. Even for chemicals RO cannot remove well, there will generally be some reduction in the concentration after the RO process. However, depending on the source water concentration RO may not remove all contaminants to below drinking water limits. This robust capability against a wide variety of contaminants is critical to the military due to the limited analytical capability in the field and the wide range of uncharacterized source water that must be used during operational deployments.

## REVIEW OF EXISTING EQUIPMENT

The development of the 600 gph ROWPU was completed in 1979. The system is a highly mobile, versatile and rugged system that may be rapidly deployed and used anywhere on the battle field. The unit uses a combination of physical and chemical treatment processes to produce potable water from any available water source. The ROWPU consists of five major systems: raw water intake, clarification, purification, distribution, and Nuclear, Biological, and Chemical (NBC) decontamination. The raw water intake typically consists of an intake strainer, a raw water pump, and the necessary hoses and valves. In the clarification system the raw water is coagulated by the addition of a cationic polyelectrolyte, then pumped through a multi-media filter followed by a set of 5 micron cartridge filters. The purification system consists of the high pressure pump, eight 6" diameter reverse osmosis elements, and a chlorine injection pump. The chlorine injection pump provides a chlorine residual required by the Army Surgeon General to ensure the water is not recontaminated during storage and distribution operations. The distribution system has 3,000 gallon collapsible fabric storage tanks, a distribution pump, a distribution nozzle, and the necessary hoses and valves. The NBC decontamination system has activated carbon and mixed-bed ion exchange filters to remove NBC contaminants from the purified water. The 600 GPH ROWPU produces up to 12,000 GPD from sources with 35,000 ppm. On waters with lower salinity, the ROWPU will produce more water. The operating day for a ROWPU is 20 hours. The remaining four hours are used for routine cleaning and maintenance. There are three models of 600 GPH ROWPUs: a trailer-mounted unit for the Army, a skid-mounted unit for the Marine Corps and Navy, and a skid-mounted unit wired for use with the bare base electrical system for the Air Force. The 600 GPH ROWPU is powered by a 30 kW generator. All versions can be transported by 5 ton truck, air transported, air-dropped, rail transported, carried on shipboard, or sling-loaded by a cargo helicopter.

The development of the 3000 gph ROWPU was completed in 1987. The system design is similar to the 600 gph ROWPU with the same five major systems: raw water intake, clarification, purification, distribution, and Nuclear, Biological, and Chemical (NBC) decontamination. Major differences include a cyclone separator mounted on the raw water pump to provide initial removal of large suspended particles. The purification subsystem includes twelve 8" diameter RO elements arrayed in two parallel streams with six RO elements in series. The water treatment system and controls are housed in a 8 foot by 8 foot by 20 foot ISO container and mounted on a 40 foot semi-trailer along with a 60 kW generator set and the high pressure pump. The system may be transported by truck, rail, ship, or air.

## REVIEW OF DEVELOPMENTAL EQUIPMENT

The 1500 gph Tactical Water Purification System (TWPS) will replace the existing 600 GPH ROWPU in the Army and U.S. Marine Corps (USMC) inventory. The design of the 1,500 GPH TWPS uses state-of-the-art technology to increase the potable water output without increasing the size, weight, or deployment features in comparison with the 600 GPH ROWPU, and to improve water production efficiency and flow rates from sources with high salinity contents. The existing 600 GPH ROWPU has insufficient water production and uses outdated pretreatment technology. The existing system is not capable of providing acceptable quantities of potable water from seawater with extremely high total dissolved solids (TDS) levels, such as those encountered during Operation Desert Shield and Desert Storm. Also, it is not capable of providing acceptable quantities of potable water from low temperature (e.g. 32 degrees Fahrenheit) water sources. The 600 ROWPU's pretreatment filters require excessive

backwashing and/or replacement when operating on turbid source waters (greater than 20 nephelometric turbidity unit (NTU)). Another consequence of operating the current system on turbid source waters is that the pretreatment system may allow colloidal particles to travel through the filters and enter the Reverse Osmosis (RO) elements. This will typically result in premature cleaning of the RO elements and may possibly cause such significant fouling that the expensive RO elements will need to be replaced.

The 1,500 GPH TWPS is a fully contained mobile water purification system consisting of seven process systems: a raw water system, a microfiltration (MF) system, an RO system, an air system, a chemical injection system, the product distribution system, and a NBC purification system. The system utilizes MF pretreatment to remove suspended solids and bacteria, and high rejection spiral wound RO membranes to produce potable water from fresh and brackish water sources as well as from salt water up to 60,000 mg/l TDS. The TWPS produces a minimum of 1500 GPH of potable water from fresh water sources, as well as a minimum of 1200 GPH from brackish, salt, and nuclear, biological, and chemical (NBC) contaminated water. The TWPS has two configurations, one for the U.S. Army and one for the U.S. Marine Corps. The Army's TWPS is mounted on a flatrack and the USMC TWPS is a skid-mounted unit, but does not include the power source (i.e. generator).

The raw water system pumps raw water from the water source to the TWPS through a floating inlet strainer with an anchor and rope, raw water suction and discharge hoses, a cyclone separator, and a static mixer. The TWPS also has an ocean intake structure system (OISS) which is used for drawing raw water through beach well point intakes for raw water sources with surf or extreme tidal conditions. MF feed water is drawn through dual 600-micron strainers, and then to each of 12 MF modules in parallel. Entering each module, the feed flows around the outside of the fibers and then through the 0.2 micron nominal membrane surface of each fiber and into the hollow core. The filtered feed water flows to the high pressure pumps that discharge to the pump end of the power recovery turbocharger where the pressure is boosted before entering the first of five RO pressure vessels arranged in a series array. Each vessel contains two 8 x 40 spiral thin film composite polyamide RO elements installed with a blanking plug between the permeate tubes. From the last vessel the concentrated feed water, now reject, discharges to the turbine side of the turbocharger where the pressure is converted to energy to run the pump side. A chemical injection system adds calcium hypochlorite to provide a residual of up to 10-mg/l free chlorine prior to discharge to one of two 3,000 gallon product distribution tanks. The NBC filter system is a separate component to be used when purifying NBC contaminated water that consists of ion exchange resin and activated carbon.

The Lightweight Water Purifier (LWP) provides the U.S. Army with the capability to produce a safe, reliable supply of potable water to support ground, amphibious, air mobile, and airborne units. The primary mission of the system is to purify water obtained from a broad range of sources, including NBC contaminated sources, to meet requirements for small military units and detachments, Special Operations Forces (SOF), and temporary medical facilities during a large range of military contingency operations to include combat, stability operations, and support operations. The LWP will be primarily transported over land in the rear compartment of the High Mobility Multi-Purpose Wheeled Vehicle (HMMWV) M1097A, and by air inside the C-130 aircraft or an UH-60 helicopter. The LWP produces 125 GPH of potable water from a fresh water source and 75 GPH of water from a seawater source. The LWP is a modular system that consists of the following process systems and modules: raw water feed system, ultrafiltration

module, high pressure pump module, RO module, chemical injection/ cleaning module, NBC post-treatment system, product water distribution system, and power source.

The raw water system consists of an electrically power feed pump, coagulant injection system and a collapsible fabric tank settling tank. The settling tank is used for the raw water source and allows suspended solids to settle to the bottom of the tank. The settling tank will reduce the solids loading on the ultrafiltration (UF) membranes thereby increasing the time between cleanings. Clarified water from the settling tank is fed to the UF Module by an electric motor driven pump. The UF module is a welded aluminum pipe frame that houses the three 0.1 micron UF membrane cartridges. The HP module houses a diesel engine driven high-pressure plunger pump that pressurizes the feedwater prior to treatment by reverse osmosis. The RO Module contains seven 2.5" diameter RO membranes in Titanium pressure vessels. The chemical injection/cleaning module houses a 20-gallon tank used for batching, mixing, and heating the cleaning solutions for the UF and RO system and to hold fresh product water. There are three, 2.5-gallon tanks for either sodium bisulfite (dechlorinating agent) or coagulant depending on the source water, antiscalant solution for the RO membranes, and a hypochlorite solution for disinfecting the product water. The NBC filter assembly consists of activated carbon to remove chemical warfare agents and ion exchange resin to remove radioactive contaminants. The system is only employed if the presence of NBC agents is suspected. The product water, after chlorination and NBC post treatment (if required) is stored in a 1000 gallon collapsible fabric tank.

## MAJOR PROBLEM AREAS

The water purification equipment developed by the military faces the challenge of treating every water source in the world while being capable of operating in extreme environments and temperatures ranging from -25°F to 120°F. The equipment must meet stringent requirements for size, weight, mobility, and transportability while being safe to operate, reliable, and easy to maintain. These systems must be operated by water purification specialists with minimal training and limited analytical equipment. Typical operation of the equipment consists of short missions where the equipment is operated at a location for 5 days where the equipment is operated continuously except for down time needed to conduct routine and scheduled maintenance, unscheduled maintenance, and preventative maintenance checks and services. The equipment is then shut down packed up and moved to another location or returned to storage until the next mission cycle. The need for a highly mobile army requires frequent shut-down and start-up cycles placing a heavy burden on the equipment, especially the RO membranes. The operational profile and analytical equipment also limit the ability to optimize the pretreatment. The requirement to operate on any water source leads to compromises in system design to enable a robust capability to treat different types of waters while sacrificing optimum performance on any specific water.

These requirements and constraints have resulted in systems which are prone to colloidal and biological fouling of the RO elements. The ROWPUs' short RO element life is directly related to the need for operating on varying water source qualities, coupled with the inherent lightweight and mobile needs of the ROWPU. Furthermore, frequent shut-down and start-up cycles due to constant relocation of the ROWPU places additional stress on the RO elements. The current operational life of the RO elements is only 200 hours. The systems are also very energy inefficient leading to high operating costs and a logistical burden in the field. The U.S.

Army and Office of Naval Research are continually seeking to improve the performance of ground based water purification systems as well as shipboard RO systems. In addition, deficiencies and new requirements in the area of military field water supply are frequently identified.

## CURRENT RESEARCH EFFORTS

The Office of Naval Research is managing an Expeditionary Unit Water Purification (EUWP) Program with the support of the Army. The program has two complementary goals in the areas of basic and applied research. The basic research goal is to identify and evaluate approaches which may significantly reduce the costs, energetics, and footprint for desalination processes. The applied research goal is to identify and develop improvements to components of large scale portable (10,000-100,000 gpd) water desalination and purification units. Specific research being conducted includes improvements to osmosis based water purification through electrodialysis/ reverse osmosis hybrid, forward osmosis, amphiphilic graft copolymer membranes, liquid crystal derived RO membranes and high flux RO membranes. Other areas being investigated include ultrafiltration improvements through pore elongation by stretching and minimizing brine disposal requirements through membrane contact distillation.

The University of Colorado is investigating the design of a hybrid RO-ED process. The concept of intimately-associating these two separation techniques is completely novel. There is no data available on the effect of pressure on the properties of electrodialysis membranes. The project will model the movement of salts (electrolytes) in a complex geometry under the influence of both pressure-driven flow and an electric field.

The University of Colorado and University of Texas are collaborating to prepare and characterize of nanoporous, composite liquid crystal membranes for reverse osmosis and desalination. Current RO membranes are amorphous, nonporous, and susceptible to chlorine attack. The LC membranes are highly cross-linked for stability, and have nanostructured ionic pathways for potentially better transport properties and salt rejection. The project will evaluate novel LC polymer membranes with ordered, ionic nanochannels for reverse osmosis and desalination applications.

Yale University and Osmotic Technologies, Inc. are investigating membrane optimization to maximize fresh water recovery with a novel forward osmosis process. The project will test, optimize, and enhance the performance of a recently developed forward osmosis (FO) process based on a new ionic solution to provide the osmotic potential that will be easily separated from the purified water. The influence of key operating parameters (pH, temperature, concentration of draw solution) on salt rejection and product water flux of the FO process will be examined.

The University of Massachusetts is investigating a new hydrolytically stable amphiphilic graft copolymers for water purification and desalination. The project will synthesize and study novel polymer materials for use as membranes in water purification applications. Polyolefins with amphiphilic character will be prepared from pendant PEG chains. Interfacially active moieties will be integrated into the polymer structure, including PEG, oligopeptides, and charged substituents. Targeted membrane features: pore size, crystallinity, impact of morphology on properties, bicontinuous structure, controlled surface properties.

The Ohio State University is investigating the development of high-flux water desalination membranes. The goal is to extend the scientific knowledge of interfacial

polymerization to high-flux membrane synthesis with hydrophilic moiety. High-flux membranes will be synthesized using pioneering interfacial polymerization with direct incorporation of hydrophilic groups. Membrane structures and transport mechanisms for high-flux membranes with hydrophilic groups will be elucidated.

The University of Texas is investigating the performance modification of ultrafiltration membranes via membrane stretching. Pore size characteristics (maximum, minimum, and mean values of the major axis, minor axis, and aspect ratio as well as surface porosity) and membrane performance (flux, rejection, and fouling) will be evaluated. A mathematical model will be developed and validated to relate final membrane structure to initial membrane structure, membrane material mechanical properties, and membrane stretching conditions.

University of Nevada is developing a direct contact membrane distillation for desalination pilot scale application and modeling a new approach for flux enhancement. The heat and mass transfer in DCMD are tightly bound. The design of a pilot-scale module for enhanced DCMD and the concurrent modeling of mass and heat transfer are essential. A new and innovative configuration of a spiral wound membrane element for enhanced DCMD will be designed, constructed, and tested. Pretreatment schemes for the protection of membranes and modules are essential for durable operation and they will be tested together with flux restoration approaches.

The Army ROWPU improvement program will consist of investigating three improvements. Improved pre-treatment systems to enhance removal of solids from the raw water and improve the quality of the feedwater to the RO elements to extend the operating life of the elements, reduce cartridge filter replacement, and increase water production. Improved RO element cleaning, preservation procedures, and chemicals to decrease frequency of element replacement, and improve long term storage of elements. New diagnostic techniques and equipment kit for identifying individual elements that are defective and need to be replaced in the field rather than replacing and disposing of all elements at once including those, which are still usable.

The Army advanced reverse osmosis work is developing technology to mitigate the effects of concentration polarization and biological fouling. To reduce biological fouling new membrane chemistries are being created by Separation Systems Technology that are resistant to chlorine. Chlorine will quickly degrade the current membrane materials. Chlorine resistant membranes will enable chlorination to eradicate the microorganisms fouling the membrane. MIOX Corporation is developing a hand held pulsed RO system with advanced spacers. Modeling has shown that pulsing the flow to the membrane will reduce the build up of contaminants at the membrane surface reducing both concentration polarization and fouling. A mechanical pulsing device is being tested to validate the modeling results. Reverse osmosis membranes most commonly come in a spiral wound element. The current spacer material is usually a diamond-patterned mesh that is rolled between layers of membrane. These meshes are not optimized to maximize flow and provide a location for fouling to occur. New spacers that can be directly printed on the membrane are being investigated. These spacers may be created in a wide variety of shapes, sizes, and heights, to improve the flow characteristics reducing concentration polarization and fouling, which are not possible to achieve in a mesh material. The pulsing and new spacer design will reduce the pressure required to operate the system and the frequency with which the system must be cleaned thus reducing operation and maintenance costs. These technologies may be applied to the whole spectrum of Army water purification systems and devices including modular small unit and individual soldier.



The Army is investigating forward osmosis as a technology for individual soldier water purification devices. The device consists of a hydration bag with an FO membrane and a nutrient or “gatorade” type solution used on the product side, which has a higher osmotic potential than the source water. Therefore osmosis occurs across the forward osmosis membrane which is similar to the RO membrane in that it allows the passage of water while rejecting materials down to the ionic level. Forward osmosis has the advantage of being a low pressure process so a system may be made out of lightweight materials and little to no external energy is required for the process since the driving force is provided by the osmotic potential of the product solution. New membrane materials are being developed along with implementation concepts and fabrication techniques to create an individual water purification system.

Atmospheric humidity is the most widely and evenly distributed source of water on earth. The mass of water available for recovery from the atmosphere is sufficient to support the soldier even in hot dry environments, but due to the low concentration the process either requires large quantities of energy to remove the water by condensation or large volumes of adsorbents to concentrate the water vapor coupled with energy requirements that are still quite significant. Conventional methods of collecting this water are too large and energy intensive applicable to battlefield requirements. In order to have military utility water from air systems must obviously be brought more in line with current water purification equipment. Promising membrane based technologies under development by the Army and DARPA will investigate new ways to condense water based on facilitated membrane transport and variable surface energy membranes. Under the facilitated membrane project membranes will be developed that act in a manner similar to biological membranes which can pump molecules across the membrane against a concentration gradient. Materials with an affinity for water can be embedded in these membranes to enhance the transport across the membrane and reduce the power requirements. In the variable surface energy project membranes are under development where the surface energy or water affinity through a pore or can be induced to change their affinity for water. In the case of the variable surface energy materials the hydrophobicity/ hydrophilicity can be varied using electric potential. A material can be made to be water loving (hydrophilic) as the source air is fed across the membrane. After the membrane is saturated with water the membrane can be converted to a water hating surface (hydrophobic) causing the water to bead up and be collectable.

The Office of Naval Research is funding a program to develop novel methods to simultaneously reduce membrane fouling (double lifetime) and increase flux (goal: x10). Fouling reduces flux, which results in frequent membrane replacement and over design of treatment system. Hydrophilic membranes lack strength but foul less, while hydrophobic membranes have mechanical integrity but foul badly. Conventional membrane are not operated at optimal flux or separation performance due to low density of pores and wide pore distribution. Performance may be improved by tailoring pore architecture, size uniformity, density, for ultrafiltration membranes with pore diameters of 2 to 1000 nm. Chemical properties of surface, bulk will be tuned for maximum durability strength and minimum fouling.

University of Colorado is developing lyotropic self-assembly, lyotropic liquid crystal polymer membranes for nanofiltration and catalytic treatment of shipboard waste water. The reactive sites will be integrated into membranes for catalytic degradation of waterborne organics into more biodegradable forms. Perfect membranes with hexagonal packing, 3.5 nm pores will be formed. The LLC-based membranes will be developed for size-selective aqueous nanofiltration.

The University of Pennsylvania is developing self-assembly, poreless two phase systems using cell membranes as a model for the rational design of multifunctional supramolecular membranes. The membranes will be developed using polymers containing tapered dendritic side groups. Cylindrical macromolecules & supramolecular networks will be used to form ion- and electron-active nanostructure systems

The Massachusetts Institute of Technology is developing block copolymer modification of phase inversion membranes using a novel polymer blend of miscible but hydrophilic and hydrophobic polymers. The objective is to fabricate water filtration membranes with increased throughput, selectivity and lifetime by increasing porosity/permeability, reducing pore size distribution, and inhibiting biological and oil fouling. The approach is to use surface modification with amphiphilic, self-organizing comb copolymer components. Where amphiphilic combs are added to the casting solution that segregate and self-organize at membrane surfaces as the phase inversion process pulls hydrophilic block to surface. Optimization of membrane morphology guided will be guided by simulation.

Membrane Technology & Research, Inc is developing poreless hydrogel coatings to enhance the performance of membranes. Hydrophilic, highly water-permeable surface coatings are being developed to create good flux/separation while reducing fouling for UF, NF, and RO Membranes. The surface coatings are based on crosslinked hydrogels that only expand 100-200%.

University of Texas is evaluating poreless fluoropolymer membranes. A novel block copolymer coating is being developed in conjunction with nonporous fouling-resistant composite nanofiltration membranes for wastewater treatment.

The State University of New York Helical is evaluating foldamers as potential membranes materials. Folding based on backbone-rigidification creates helices with large cavities. A covalently linked backbone whose rotational freedom is limited by an additional set of non-covalent bonding (bifurcated or 3-centered H-bonds) leads to a globally folded structure based on localized rigidification. The crystal structure reveals a helical conformation. Large, hydrophilic, cavities with tunable sizes are created. This tunability is seen in few natural or unnatural systems. The hollow helices are assembled into anisotropic, nanoporous membranes Biomimetry used to design molecules that force helical conformations.

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